FOURIER TRANSFORM SPECTROMETRY IN THE ULTRAVIOLET-VISIBLE REGION

By

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An investigation of the analytical merits of Fourier transform spectrometry, at short wavelengths, was made using a Michelson interferometer capable of operation in the ultraviolet-visible region (UV-Vis). The multiplex effect on signal-to-noise ratio was examined. Advantages and disadvantages of Fourier transform spectrometry in the UV-Vis relative to conventional spectrometry are discussed.

A review of the use of the Michelson interferometer for spectroscopic purposes and for Fourier transform spectrometry is presented. The interferometers currently available for operation in the UV-Vis are described.

Molecular absorption measurements were made using an interferometer and a diffraction grating. This approach did not have significant advantages over conventional methods and the multiplex disadvantage degraded signal-to-noise ratio. Detection limits are given for some polycyclic aromatic compounds (PAC).

Molecular fluorescence measurements of PAC frozen in a Shpol'skii solvent at 77K were performed by Fourier transform spectrometry. Emission spectra were acquired by using a monochromator to select the excitation radiation and a cutoff filter after the interferometer. Excitation spectra were acquired by passing broad-band, ultraviolet radiation through the Michelson interferometer onto the frozen sample. The detection limits from the emission spectra were sufficiently poor to prohibit analytical use. Detection limits obtained from the excitation spectra were comparable to conventional methods, in some cases even better, due to the use of broad-band excitation.

A Fourier transform spectrometer for continuum-source, atomic absorption measurements was constructed and evaluated. Degradation of signal-to-noise ratio due to the multiplex effect was reduced by using a grating for dispersion of the radiation before the interferometer. Continuum radiation passed through a flame containing the analyte. A 5 nm window of radiation, centered around the absorption lines of interest, was collected and passed through the interferometer onto a photomultiplier tube. Detection limits using the interferometer were poorer than conventional measurements, but a few advantages were realized. Complete absorption line profiles were acquired, including measurements of the true background in the region of absorption. Calibration curves were extended by using the line profile. Wavenumber accuracy was high and spectral resolving power could be easily modified.

FOURIER TRANSFORM SPECTROMETRY

Historical Overview

Fourier Transform Spectrometry uses the interferometer that was designed in 1881 by A. A. Michelson.[1] He first constructed the interferometer for purposes other than spectroscopic, but before the end of the nineteenth century he had devoted much time to spectroscopic interferometry. Michelson's use of the interferometer, and the rediscovery of the interferometer in the 1950s, are responsible for the widespread use of Fourier transform spectrometry.

Michelson's first experiment with his interferometer was to test for the existence of the ether—the stationary, luminiferous medium through which light waves were thought to travel. He sent, at exactly the same time, a beam of light a fixed distance in one direction, and a second beam of light the same distance at a right angle. The two beams were reflected by mirrors and combined at the starting point.

Michelson reasoned that if the two beams returned at the same time, then no interference pattern would be observed. The stationary ether could not exist. However, if one of the beams travelled with the flow of the earth through the ether, and the other perpendicular to the flow, then the beams would return at slightly different times. An interference pattern would be observed and existence of the luminiferous ether would be demonstrated.

With great care to stabilize the interferometer, Michelson made several attempts to observe the delay that the ether would produce in one beam of light. Those famous experiments yielded a null result—no interference pattern was ever observed—and the existence of the ether was refuted.

By 1888 Michelson was using the interferometer for spectroscopic purposes. Long before numerical algorithms were available to decipher the information contained in the complex interferograms, Michelson was using interference patterns (visibility curves) to observe hyperfine structure in spectral lines. He proposed the use of atomic radiation as a standard of length when he noticed the narrow spectral width of a red cadmium line, and he was the first to propose the existence of the Balmer doublet of hydrogen. Each was a result of visually inspecting the interference patterns in his interferometer.

After Michelson, and before the advent of computers, interferometry and the use of the Michelson interferometer were rare in spectroscopy. The direct methods of obtaining high-resolution, spectral information with a dispersive spectrometer replaced the disagreeable method of interferometry. Any advantages of interferometry that would be manifested by the Fourier transformation were hidden in its complexity.

Michelson realized the limitations of visual inspection and intuition. Simple spectral features could be obtained from visibility curves, but retrieving information in the presence of complex light sources was almost impossible. To simplify the visibility curves, he used a predispersing element, a prism spectroscope, to allow only a portion of the radiation to enter the interferometer. "This is necessary because the spectra of most substances consist of numerous lines. . . . It is usually better to

separate the various radiations before they enter the interferometer."[2] This trick would be rediscovered in the 1980s.[3]

Michelson built an analog computer to help decode his visibility curves. Recognizing that the observed interference pattern is the sum of many harmonics, he built a mechanical device for adding up to 80 harmonic oscillations and displaying the resultant harmonic waveform. By choosing the harmonics he created synthetic visibility curves to compare with those experimentally obtained. Compared to Fourier transform spectrometry, which extracts spectral information from the interference pattern, the harmonic analyzer worked backward; the interference pattern was fabricated from an artificial spectrum. Michelson realized, however, the power of his interferometer to resolve fine spectral features.

Not until the 1950s were the combined capabilities of interferometry and Fourier transformation realized. Fourier transformation was shown to be a suitable, if elaborate, method of decoding the spectral information contained in the interference pattern. In 1951 the Fourier transform was first applied to data from a Michelson interferometer.[4] The increasing application of computers soon made the calculations routine. Only one more feature was needed to make interferometry attractive to spectroscopists.

In the 1950s, several researchers pointed out the advantages of interferometry over conventional spectrometry. Jacquinot noticed that because an interferometer has a circular geometry, and a conventional spectrometer uses slits, there is a light throughput advantage.[5] Fellgett demonstrated the multiplex effect, an advantage that arises in interferometry because the detector views the entire signal during the

recording time. These advantages, and several others, revived interest in the technique. They are described in more detail in a section below. Fourier transform spectrometry was shown to be more than a spectroscopic curiosity; it actually worked better than conventional spectrometry in some cases.

Fourier Transformation

A simplified diagram of a Michelson interferometer is shown in Figure 1. Most interferometers used in Fourier transform spectrometry are simply better instrumental implementations of the first Michelson interferometer.

The phase difference between the two beams of radiation which creates the interference is introduced by separating the incident radiation and by using unequal pathlengths. The amplitude division of the radiation is accomplished by dividing the incident radiation with a semi-transparent beamsplitter. One beam travels a fixed pathlength to a stationary mirror and is reflected. The second beam travels a variable pathlength to a movable mirror and returns. The two beams recombine at the beamsplitter, with constructive and destructive interference depending on the introduced phase delay.

To illustrate the interference effect, monochromatic radiation simplifies the explanation. When the path difference (retardation) between the two legs of the interferometer is zero or a multiple of λ, where λ is the wavelength of the incident radiation, the recombining beams are exactly in phase and interfere constructively. The intensity of the radiation at the detector is the sum of the intensity of the two beams. All of the radiation goes to the detector and none returns to the source.

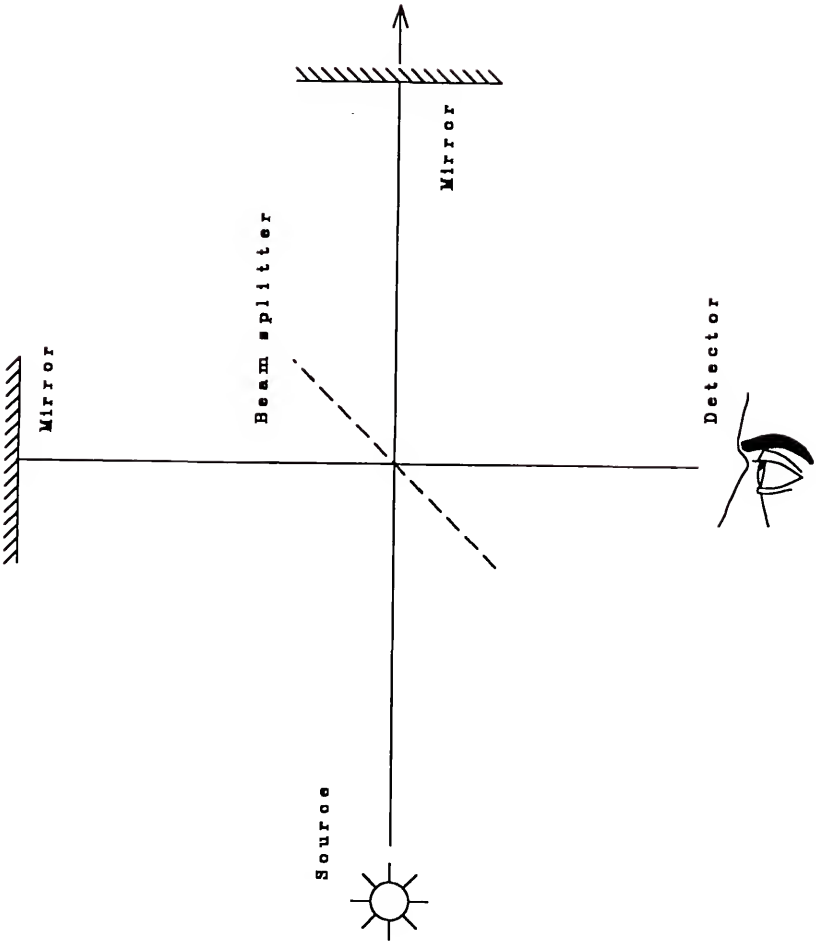

Figure 1. Michelson interferometer.

When the retardation is a multiple of $\frac{1}{2}\lambda$, the beams will be exactly 180° out of phase and will interfere destructively. The intensity of radiation at the detector will be zero. All of the radiation returns to the source.

If the movable mirror in the interferometer is moved at a constant rate away from the zero retardation point, the recombining beams will undergo periodic destructive and constructive interference. For a monochromatic source of radiation the signal at the detector (the interferogram) will vary sinusoidally. For polychromatic radiation the detector signal will depend on the individual sinusoidal variations. The signal will be a composite of the component interferograms.

The intensity at the detector, I(x), can be expressed as a function of the retardation, x (cm):

$$I(x) = \tfrac{1}{2}I(\sigma)\ [1 + \cos\ 2\pi\sigma x]$$

where $I(\sigma)$ is the intensity of the source radiation, and σ is the frequency of the radiation (cm^{-1}). The frequency of the sinusoidal signal at the detector depends on the frequency of the incident radiation, σ, and on the rate of change in the retardation, x. The intensity of the signal depends on the intensity of the radiation.

This simple relationship is complicated by nonidealities in practice. The beamsplitter may not be exactly 50% reflecting and 50% transmitting, and its efficiency often varies with the frequency of the radiation. An experimentally determined factor that depends on σ is often used for correction of the acquired interferograms. Other imperfections that may

arise with a dependence on radiation frequency are variations in detector response and instrumental response.

In the above equation, I(x) is defined as the cosine Fourier transform of $I(\sigma)$. The Fourier theorem shows that the reverse is also true. $I(\sigma)$ is the cosine Fourier transform of I(x). The Fourier transform of the interferogram signal obtained at the detector, I(x), is the intensity of the radiation, $I(\sigma)$.

In essence, the spectral information of $I(\sigma)$, the intensity of radiation at a particular frequency, is encoded in the sinusoidal signal at the detector. In this way it is an indirect method when compared to conventional spectrometry which measures $I(\sigma)$ explicitly. Michelson decoded the observed interferograms by experienced inspection but was unable to work with complicated interferograms. In Fourier transform spectrometry this information is decoded by numerical means, by the Fourier transform.

A thorough explanation of the application of the Fourier transform exists.[6] A simple discussion is sufficient for an understanding of the operation of Fourier transform spectrometry in the ultraviolet-visible.

To apply the Fourier transform, each point in the interferogram is multiplied by a cosine function of a given frequency and of unit intensity. The frequency of the cosine function is varied during the deciphering process. If the interferogram does not contain a component at that frequency, then the result will be zero. If the frequency of the function corresponds to a component harmonic of the interferogram, then the result will be a cosine wave, the magnitude of which is equal to the intensity of the radiation at that frequency.

The relationship between the two domains, between the spectral information and the detector signal, can be expressed mathematically. When polychromatic radiation is passed through the interferometer, the signal at the detector is the sum of the individual sinusoidal signals:

$$I(x) = \int_{-\infty}^{+\infty} I(\sigma) \cos 2\pi\sigma x \, \delta\sigma + \text{constant}$$

The useful feature of the Fourier transform is the reciprocal relationship:

$$I(\sigma) = \int_{-\infty}^{+\infty} I(x) \cos 2\pi\sigma x \, \delta\sigma + \text{constant}.$$

This expression relates the intensity of a spectral component to the interferogram at the detector. The Fourier transform converts from one domain (retardation, x) to a reciprocal domain (frequency, σ) which is more practical. If x is measured in cm, then σ is in cm^{-1}.

In practice the measurement is more complicated. The relationship between $I(\sigma)$ and I(x) implies that spectral information can be obtained over the entire range from $-\infty$ to $+\infty$ cm^{-1} (really from 0 to $+\infty$) with infinitely-high resolving power. This would require a retardation of ∞ cm, with an infinite number of measurements. The restriction of moving the mirror a finite distance, and of collecting a manageable number of data points, limits the resolution and spectral range.

In comparison to conventional spectrometry, spectral information is obtained in a roundabout way. Spectral information contained in the incident radiation is encoded by the Michelson interferometer. The constructive and destructive interference pattern which appears at the detector contains all of the spectral information in a single signal. That signal is a composite of many sinusoidal signals which are varying individually. The Fourier transform decodes the spectral information by transferring the signal from one domain to another. In Fourier transform spectrometry the transformation is from the displacement domain to the spectral domain.

The calculations to perform the Fourier transform on the interferogram are sufficiently complex and numerous to require the computing capability of a mini-computer. To reduce the calculation time to under a minute, algorithms have been devised.[7] Today, the actual Fourier transformation is often a transparent operation to the spectroscopist.

Advantages

Michelson used the interferometer at an early date to predict hyperfine splitting of atomic emission lines before any method of observation existed, but interferometry remained a complicated and indirect method for obtaining spectral information. At the beginning of the twentieth century, high-resolution spectrometers were available, capable of measuring highly resolved spectra directly. Not until the 1950s, when advantages of interferometric techniques were first demonstrated, was the Michelson interferometer and Fourier transformation recognized as a powerful spectroscopic tool.

P. B. Fellgett, in 1951, pointed out in his thesis the signal-to-noise ratio advantage that arises from the multiplex nature of interferometry compared to dispersive spectrometry.[4] It is now called the multiplex advantage or Fellgett's advantage, and it appears because the interferometer allows the entire spectral band to be viewed by the detector for the duration of the measurement period. This signal-to-noise advantage is great enough to warrant the use of interferometry in cases where it applies.

Figure 2 compares dispersive spectral acquisition with multiplex acquisition. A dispersive technique divides the spectrum into N resolution elements, determined by the resolving power of the spectrometer. If the total time of spectral acquisition is T, then each resolution element is sequentially observed for a time T/N in a dispersive technique. A multiplex technique, such as Fourier transform spectrometry, observes each resolution element for the entire measurement period, T. The multiplex technique, then, views each element for a factor N longer than a dispersive technique.

For detector-noise limited systems, the signal for each element is proportional to the time of spectral integration: T/N for the dispersive case and T for the multiplex case. The noise for each element is proportional to the square root of the time of integration: $(T/N)^{\frac{1}{2}}$ for dispersive and $T^{\frac{1}{2}}$ for multiplex. The ratio of the signal to the noise is $(T/N)^{\frac{1}{2}}$ for dispersive and $T^{\frac{1}{2}}$ for multiplex. For equal spectral acquisition time, T, the multiplex technique should have a signal-to-noise ratio advantage of $N^{\frac{1}{2}}$.

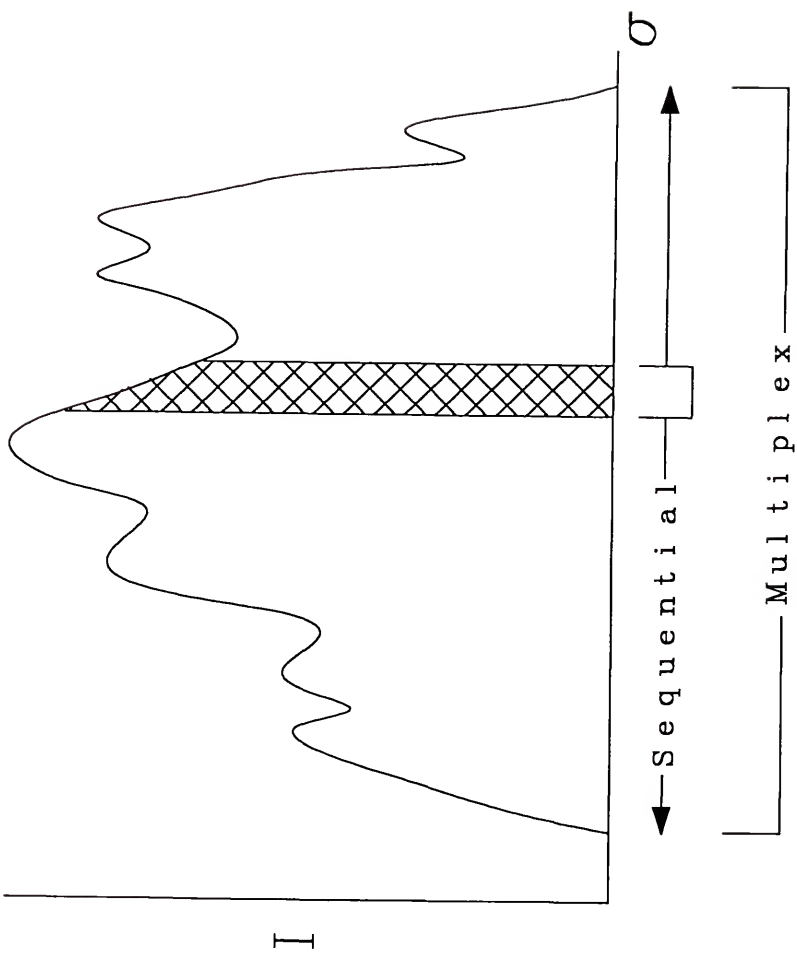

Figure 2. Sequential vs. multiplex spectral acquisition.

Fellgett's advantage appears only when the detector is the limiting source of noise, when the noise is not proportional to the intensity of the radiation. This restriction is fulfilled in the infrared region, where detectors are thermal or photo-conductive devices and inherently noisy compared to the radiation source. In this region Fellgett's advantage is fully realized, and for this reason, Fourier transform spectrometry in the infrared is popular.

In regions of shorter wavelength, in the ultraviolet-visible region, the detectors are photoemissive devices and are not the limiting sources of noise. In these regions the spectroscopic systems are usually limited by the source noise.

For source shot noise, the noise is proportional to the square root of the signal. A multiplex technique in the ultraviolet-visible region, with a signal N times larger than a dispersive technique, will also be $N^{\frac{1}{2}}$ times more noisy, exactly cancelling Fellgett's signal-to-noise advantage of $N^{\frac{1}{2}}$.

For source fluctuations, the noise is directly proportional to the signal. A multiplex technique in the ultraviolet-visible region, with a signal N times larger, will be N times more noisy, resulting in a net signal-to-noise disadvantage of $N^{-\frac{1}{2}}$.

In practice, the multiplex effect results in a disadvantage in the ultraviolet-visible region that depends on the nature of the signal. For dense spectra, when the analyte signal is weak compared to the non-analyte signal, the signal-to-noise ratio can be small. The noise from the non-analyte signal is distributed to the weak analyte signal. For sparse spectra, the multiplex effect is expected to degrade the signal-to-noise ratio to a lesser extent.

The multiplex effect on the signal-to-noise ratio has been discussed in the literature.[8] The signal-to-noise ratio for a multiplex technique is defined with regard to the limiting noise. In detector noise limited cases (as in the infrared) the expression is given by

$$(S/N)_m = \frac{\frac{1}{2} R_a T}{\sqrt{R_n T}} = \frac{\sqrt{T}}{2} \frac{R_a}{\sqrt{R_n}}$$

where R_a is the analyte count rate (s^{-1}) and R_n is the detector dark count rate. The expression for a dispersive technique is given by

$$(S/N)_d = \frac{R_a T/N}{\sqrt{R_n T/N}} = R_a \sqrt{\frac{T}{R_n N}} .$$

The ratio of the two is an expression for the multiplex effect when the system is limited by detector noise:

$$A = \frac{(S/N)_m}{(S/N)_d} = \frac{\sqrt{N}}{2} .$$

The factor of two appears because half the source radiation in an interferometer is returned to the source. A multiplex advantage appears when N is greater than 4, or when the number of elements viewed in the dispersive technique is greater than 4. Unfortunately, detector noise limited systems seldom occur outside the infrared.

For the case where the noise in the above expressions is determined by the photon shot noise in the background, then a slight disadvantage ($A < 1$) appears. For fluctuation noise in the background then A can be significantly less than 1, a serious disadvantage. In the ultraviolet-visible region the multiplex effect will depend on which noise source is limiting.

Fellgett's advantage, or any net multiplex disadvantage that results in interferometry, cannot be the driving force for using Fourier transform spectrometry in the ultraviolet-visible region. However, there are other advantages when interferometry is compared to conventional spectroscopic techniques.

One of those advantages was demonstrated by P. Jacquinot in 1954.[5] Jacquinot's advantage refers to the greater throughput (or light transmission) of an interferometer compared to a dispersive spectrometer of equal resolving power.

For a spectrometer or an interferometer, the throughput depends on the resolution. When an interferometer has resolving power equal to that of a dispersive spectrometer, the throughput advantage can be one or two orders of magnitude. The advantage arises from the geometry of the instruments.

Resolving power is defined as $R = \sigma/\delta\sigma$. In a dispersive spectrometer R is limited by the width of the dispersive grating and the slit width. In an interferometer R is determined by the area of the mirrors and detector, and the aperture area. The circular geometry of the interferometer entrance aperture results in a throughput advantage for the same resolving power.

Throughput, Θ, is defined as the product of the solid angle of the incident beam, Ω (sr), and the area of the beam that is viewed by the detector, A (cm^2):

$$\Theta = A\,\Omega, \quad cm^2\ sr$$

The maximum throughput of a Michelson interferometer is given by

$$\Theta_I = 2\pi\ A_I\ \frac{\Delta\sigma}{\sigma_{max}}, \quad cm^2\ sr$$

where A_I is the area of the mirrors. The throughput of a grating spectrometer is given by

$$\Theta_G = \frac{h\ A_G\ \Delta\sigma}{f\ \sigma^2} \quad cm^2\ sr$$

where A_G is the area of the grating, h is the slit height, and f is the focal length.

Jacquinot's advantage is the ratio:

$$\frac{\Theta_I}{\Theta_G} = \frac{2\pi\ A_I\ \Delta\sigma\ /\ \sigma_{max}}{h\ A_G\ \Delta\sigma\ /\ f\ \sigma^2} = \frac{2\pi\ A_I\ f\ \sigma^2}{h\ A_G\ \sigma_{max}}.$$

The limitation of the dispersive spectrometer is apparent from the above equation. To achieve the same resolution as the interferometer, narrow slits must be used. A_G is small compared to A_I.

Jacquinot's advantage appears in all regions, whether the system is detector noise limited or source noise limited. However, in the ultraviolet-visible region, Jacquinot's advantage may be completely overcome by a multiplex disadvantage.

Connes' advantage refers to the accuracy and precision with which Fourier transform spectrometry can measure spectral frequency. An internal monochromatic source of radiation can be used as a reference. Precise measurement of the calibration frequency can be performed as long as the reference source is not moved. Frequency accuracy can also be very high, and external calibration against a source of known frequency is possible for extreme accuracy.

The most important feature of a Michelson interferometer, when considering operation in the ultraviolet-visible region, is the high resolving power. The resolution of a Michelson interferometer varies with the movement of the mirror, $R = 2L\sigma$, where L is the path difference. The resolving power of a Michelson interferometer can approach $R = 10^6$, which can only be achieved by the best, dispersive instrument. The resolving power can also be easily adjusted to suit the application, by varying the length of mirror travel.

The analytical applications that fully utilize the high resolving power of Fourier transform spectrometry will realize an advantage of the Michelson interferometer in the ultraviolet-visible region. The simultaneous wide-range spectral acquisition that is possible may be an advantage, but this multiplex effect will also result in a signal-to-noise disadvantage.

Use in the Ultraviolet-Visible Region

The researchers who in the 1950s discovered the advantages of interferometry were most interested in operation in the ultraviolet-visible region. Michelson certainly was limited to the visible region. However, few modern interferometers have been designed for operation at short wavelengths.

Almost all of the Michelson interferometers used today in Fourier transform spectrometry are designed for operation in the infrared region. Fellgett's multiplex advantage is the driving force. Although Jacquinot's throughput advantage does appear at shorter wavelengths, the multiplex effect can cause a signal-to-noise disadvantage when measurements are not detector noise limited. The few interferometers that do operate in the ultraviolet-visible region are used mainly for physical rather than analytical studies.

A Michelson interferometer designed for the ultraviolet-visible region is conceptually no different from the commercial, infrared interferometers. Appropriate optics must be selected for different spectral regions, but the basic design is the same. Technically, however, the construction of an ultraviolet-visible interferometer is difficult. Tolerances must be reduced as the wavelength decreases. Stability and optical flatness to $\frac{1}{4}\lambda$ must be maintained throughout the scan.

One of the first modern interferometers for use in the ultraviolet-visible region was built by Horlick and co-workers.[9-12] To achieve the necessary stability the moving mirror was driven on an air-bearing suspension system, which prohibited its use in the vacuum-ultraviolet. The stability of the drive mechanism was satisfactory for maintaining alignment to 200 nm with modest resolution.

Horlick demonstrated the use of Fourier transform spectrometry in the ultraviolet region by measuring atomic emission from an inductively-coupled plasma and from hollow-cathode lamps. The signal-to-noise degradation that resulted from the multiplex effect was significant, and detection limits were one or two orders of magnitude poorer than with a conventional spectrometer. Attempts were made to reduce the spectral bandpass of the radiation entering the interferometer to reduce the multiplex effect.

Three research interferometers with high resolving power have been constructed for the ultraviolet-visible region. One was a stepped-scan interferometer in Orsay, France, that used cats-eye reflectors[13], and the other a 1 m interferometer at Kitt Peak.[14-16] The Kitt Peak interferometer also uses cats-eye reflectors to maintain optical alignment by minimizing tilt. High-resolution measurements of atomic emission and inductively-coupled plasma emission were performed with the systems. Signal-to-noise is poorer than with a conventional system, but other advantages of Fourier transform spectrometry made the measurements worthwhile, especially for physical studies at high resolution. A third interferometer with even higher resolving power (5 m) has been constructed at Los Alamos National Laboratory using the same instrumental design.

Two Michelson interferometers that work in the ultraviolet-visible region are commercially available, and one of them (Bomem) was used in the current study. Chelsea Instruments makes a Fourier transform spectrometer that was designed by A. P. Thorne and is capable of operation to 180 nm.[17] In principle it is very similar to the interferometer made by Bomem, Inc., except that the Chelsea instrument uses cats-eye reflectors for stability.

The Bomem instrument uses a method of dynamic alignment. By continuously monitoring the interferogram during the scan it adjusts the mirrors to maintain alignment.

Both interferometers avoid undersampling of the interferogram (aliasing) by dividing the fringes of the 632.8 nm HeNe laser. The frequency of the laser used for reference is 15798 cm^{-1}. To accurately sample an interferogram the upper limit on the spectrum is 15798 cm^{-1}, or 632.8 nm. To go beyond this limit the interferogram is sampled 8 times for each HeNe fringe, enabling a spectral range to 63192 cm^{-1}. The data set generated by this method is enormous and is reduced by real-time filtering.

The Bomem interferometer that was used in the current study is capable of operation from 222 nm in the ultraviolet to 2 mm in the far-infrared. The interferometer is of conventional design, with flat mirrors at the two legs of the interferometer. The moving mirror is driven by a steel belt attached to a direct torque motor. During the acquisition of the interferogram the alignment is dynamically maintained by monitoring the HeNe interferogram from three paths through the interferometer. Servo mechanisms adjust the tilt of the mirrors during the scan.

FOURIER TRANSFORM MOLECULAR ABSORPTION SPECTROMETRY

Introduction

Fourier transform spectrometry in the ultraviolet-visible region, because it is source shot noise limited, can have a signal-to-noise ratio disadvantage compared to dispersive spectrometry, especially with dense spectra.[8] At the expense of poorer signal-to-noise ratio, Fourier transform spectrometry can be satisfactory for high resolution measurements.[18,19] However, low-resolution spectroscopic studies, such as molecular absorption measurements, are not expected to be performed with advantages over conventional methods. The broad, dense spectra with high intensity throughout a wide spectral range should show a significant signal-to-noise ratio degradation compared to dispersive spectrometry. To investigate these expectations, a Michelson interferometer was used to obtain low-resolution, molecular absorption spectra of polycyclic aromatic compounds (PAC).

The molecular absorption bands of PAC are in the ultraviolet region, and any source radiation outside of these bands that reaches the detector will contribute to the noise of the system. Filters can sometimes be found to correspond to the region of interest, but this method of limiting the radiation is not versatile. In this work, a plane grating was used to select the lamp radiation that entered the interferometer, as previously suggested.[3,14] The spectral window of radiation that passed

through the sample cell and onto the detector could be selected to match the absorption band of the sample.

Experimental

Figure 3 shows a schematic diagram of the experimental setup used for this study. It was similar to a conventional spectrophotometer in most respects. The Michelson interferometer replaced the spectrometer.

A 150 W xenon arc lamp (ILC Technologies, Sunnyvale, CA) was used as the excitation source. This lamp has high radiant output in the ultraviolet-visible region and uses an integral parabolic reflector for collecting and collimating the radiation.

Collimated radiation from the source was diffracted by a plane-ruled grating with 600 lines/mm (SLM-Aminco, Urbana, IL). An iris diaphragm passed only a portion of the dispersed radiation (approximately 70 nm FWHM). A quartz lens focused the radiation on a second aperture at the entrance port of the interferometer (DA3.02, Bomem Inc., Vanier, Quebec). The use of the grating added some versatility to the system. The grating could be rotated to select the excitation region of interest, while excluding any radiation that would simply add noise by the multiplex effect.

The absorption cells were 1 cm quartz cuvettes. The cuvettes were mounted in the sample compartment of the interferometer, with an aperture to block the HeNe laser radiation that is used for alignment in the interferometer. An elliptical reflector (Bomem) collected the radiation transmitted through the cell and focused it onto an end-on photomultiplier tube (R647, Hamamatsu). No filters were used.

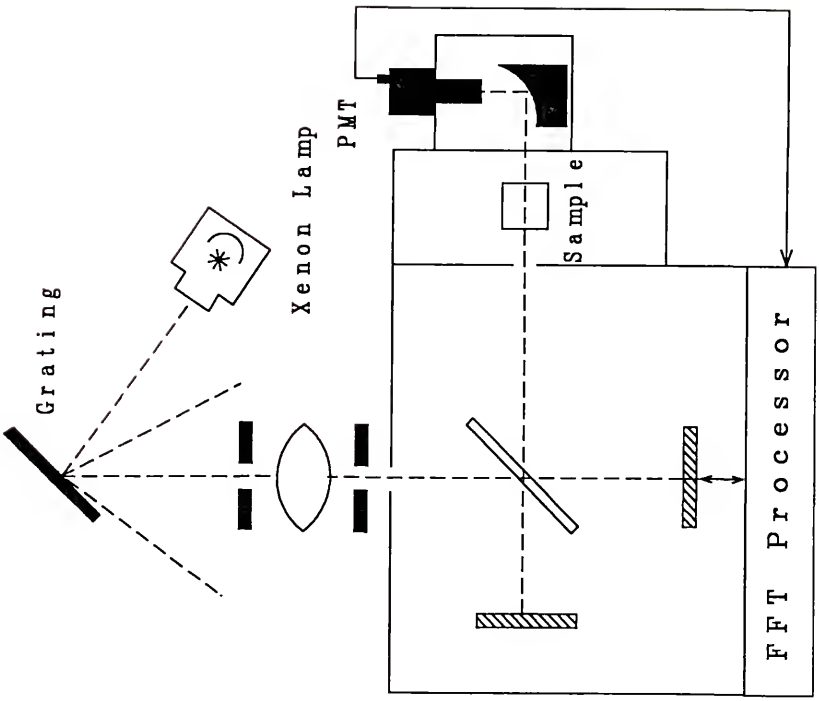

Figure 3. Schematic of molecular absorption setup.

Each reference spectrum was obtained by adding 1000 interferograms with an instrumental resolution of 64 cm^{-1}. The sample absorption spectra were obtained by coaddition of 100 interferograms. The scan rate of the interferometer mirror was 0.15 cm/s. At this rate, the time of spectrum acquisition was approximately 5 min.

Results and Discussion

The absorption spectrum of benzo(a)pyrene is shown in Fig. 4. For the complete acquisition of the absorption spectrum, two measurements were made using two different windows of excitation radiation. The separate measurements were then linked by the computer. In Fig. 4, the arrow points to the point at which the spectrum was connected.

One of the disadvantages of this approach was apparent. Much of the multiplex effect was destroyed by using a predispersing element to select a 70 nm window. The signal-to-noise degradation is reduced, but the information that can be obtained in one pass was limited.

The profiles of the excitation radiation used for the measurements are shown above the benzo(a)pyrene absorption spectrum. The relative intensity of the two windows is indicated by the magnitude of the curves. The source profiles were obtained by using solvent blanks and by rotating the grating until the window of radiation was centered on the region of interest. They were used as the reference spectra for the absorption measurements. Calibration of the grating position was not necessary, because the interferometer provided an absolute wavenumber reference.

Several analytical figures of merit were calculated for the absorption measurements of the PAC and are listed in Table 1. The limit of detection

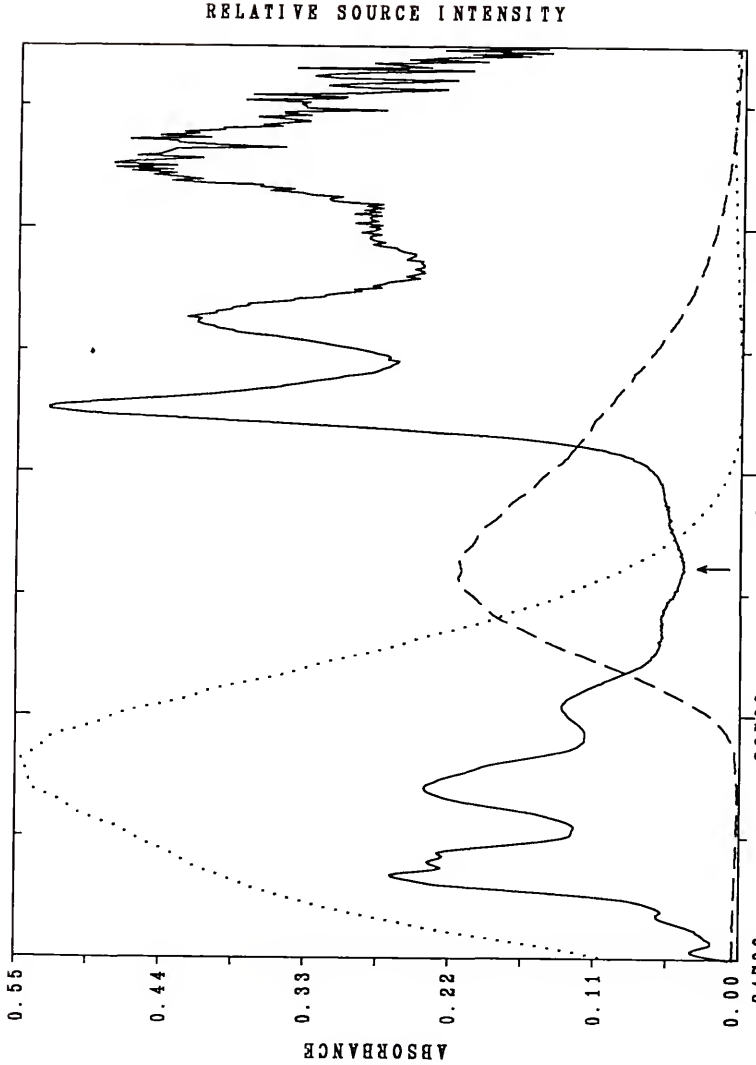

Figure 4. Combination of two absorption spectra of benzo(a)pyrene (100 ppm) in hexane. Source intensity functions are shown in broken lines.

was calculated as the sample concentration having an absorbance equal to three times the standard deviation of the blank (σ_{bl}). One hundred interferograms were coadded for each blank measurement, and σ_{bl} was calculated with 16 blanks. For a conventional spectrophotometer, σ_{bl} may vary from 10^{-3} to 10^{-5} absorbance units, depending upon the particular instrumental parameters.[20] Assuming $\sigma_{bl} = 10^{-3}$ and the molar absorption coefficients given in Table 1, the detection limits for benzo(a)pyrene and benzo(ghi)perylene expected with a conventional instrument would be 30 ppb and 15 ppb. These detection limits are an order of magnitude better than those obtained by Fourier transform spectrometry.

Since the present system should be shot noise limited,[22] the signal-to-noise ratio is expected to be directly proportional to the square root of the source intensity, and to the square root of the integration time (or number of spectral coadditions).[22,23] Flicker noise should remain localized to the generating spectral region.[22,24]

The degradation in signal-to-noise ratio with source intensity decrease is evident in Fig. 4. The spectrum becomes significantly noisier beyond 36000 cm^{-1}, where the source intensity is low. An increase in source intensity should result in improved detection limits. This could be accomplished by using a source with a higher ultraviolet output, such as a 300-1000 W xenon arc lamp. Better collection optics between the source and interferometer could also improve the radiation intensity at the sample. Replacing the grating with a quartz prism would increase the intensity, because all diffraction orders could be collected. However, the effect of increased throughput would be partially compensated by the multiplex effect.

TABLE 1

Fourier Transform, Molecular
Absorption Measurements

	Peak λ (nm)	LOD[a] (ng/mL)	Average %RSD[b]	Measured ε (L/ mol cm)	Literature[21] ε (L/ mol cm)
Benzo(a)pyrene	383.7	500	8.4	26,569	26,500
Benzo(ghi)perylene	288.2	800	3.3	42,600	43,400
Benzo(ghi)perylene	299.4	300	2.8	54,200	59,700

[a]100 coadditions

[b]n = 3

To check the dependence on integration time, signal-to-noise ratio measurements taken with coadditions of 100 and 1000 were compared to the signal-to-noise ratio found for a single scan. The signal-to-noise ratio was calculated as the mean absorbance signal over a given spectral range, divided by the standard deviation in the absorbance values across that range. When the coadditions were increased by a factor of 100, the signal-to-noise ratio was found to increase by a factor of 10.3 ($\approx \sqrt{100}$). When the number of coadditions was increased to 1000, a factor of 19.5 increase in signal-to-noise ratio was observed ($< \sqrt{1000}$). This indicates that some long-term noise, such as source fluctuations, were contributing at long integration times. A factor of two can be gained in the signal-to-noise ratio if the number of coadditions for each sample is increased from 100 to 1000. The time of acquisition increased by a factor of ten.

Using a grating or prism to select a band of excitation radiation has advantages. The multiplex disadvantage is minimized by a reduction of the extraneous radiation at the detector. Filters do not have to be obtained for each region of interest, and choosing the region can be automated. The relatively low dispersion of the grating used here resulted in a broad excitation band (70 nm), and a higher-dispersion grating could be used to give smaller bands of exciting radiation. For those studies in which a smaller excitation bandwidth is more suitable, such as continuum-source atomic absorption,[17] the use of a grating with higher dispersion would be appropriate. Reducing the bandwidth of the exciting radiation at the detector would improve the signal-to-noise ratio.

FOURIER TRANSFORM MOLECULAR FLUORESCENCE SPECTROMETRY

Introduction

Fourier transform spectrometry has greatest advantage when the signal measurements are limited by the detector noise, as they are in the infrared region. The multiplex advantage which appears in the infrared is usually not realized when measurements are made in the ultraviolet-visible region, where the system is limited by the photon shot noise. The shot noise in the total signal is uniformly distributed throughout the ultraviolet-visible spectrum and negates Fellgett's multiplex advantage.[25] Where the spectral component of interest is weak relative to the mean spectral intensity, there can even be a multiplex disadvantage.[8,26] Dense spectra, such as those in absorption spectroscopy, have a lower signal-to-noise ratio in regions of low intensity. Source flicker noise, which is dependent on the frequency and not uniformly transferred over the spectrum, can further degrade signal-to-noise ratio and spectral resolution.[22] Only in a few cases will there be a signal-to-noise advantage in the ultraviolet-visible region. When a spectrum is sparse, such as an emission spectrum, and the line of interest is more intense than the mean spectral intensity, then there will be a signal-to-noise ratio advantage.[27]

To minimize the effect of shot noise on an ultraviolet-visible spectrum, the detector can be blinded to portions of the spectrum. If only the line of interest reaches the detector, then there can be no

multiplex disadvantage. One way of minimizing unwanted radiation reaching the detector is to place a low-resolution monochromator before the interferometer to allow only a small window to be viewed.[3] The signal-to-noise ratio is improved, but much of the multichannel detection capability is lost. An alternative approach is to limit the spectral bandpass after the interferometer and before the detector.

Low-resolution molecular spectroscopic studies with large spectral windows are expected to have a multiplex disadvantage. Shot noise from the dense spectra will be distributed over the entire region, increasing detection limits and obscuring weak spectral features. In this study, a Michelson interferometer was used to acquire molecular fluorescence excitation and emission spectra with low resolution. The spectra of coronene and other PAC in frozen Shpol'skii solvents were obtained by limiting the spectral bandpass of radiation reaching the detector. Optical filtering was necessary for satisfactory results. The effects of the multiplex technique on the quantitative determination of these compounds will be discussed.

Experimental

A schematic diagram of the fluorescence emission system is shown in Fig. 5. The source was a 150 W compact xenon-arc lamp (ILC Technologies, Sunnyvale, CA), operated at 14 A. Radiation from the lamp was focused on the entrance slit (1 mm) of a small monochromator (H-10, Jobin-Yvon), to select a band of ultraviolet radiation for excitation. The excitation radiation was incident on a quartz Dewar flask (SLM-Aminco, Urbana, IL) filled with liquid nitrogen. Samples were contained in quartz tubes and

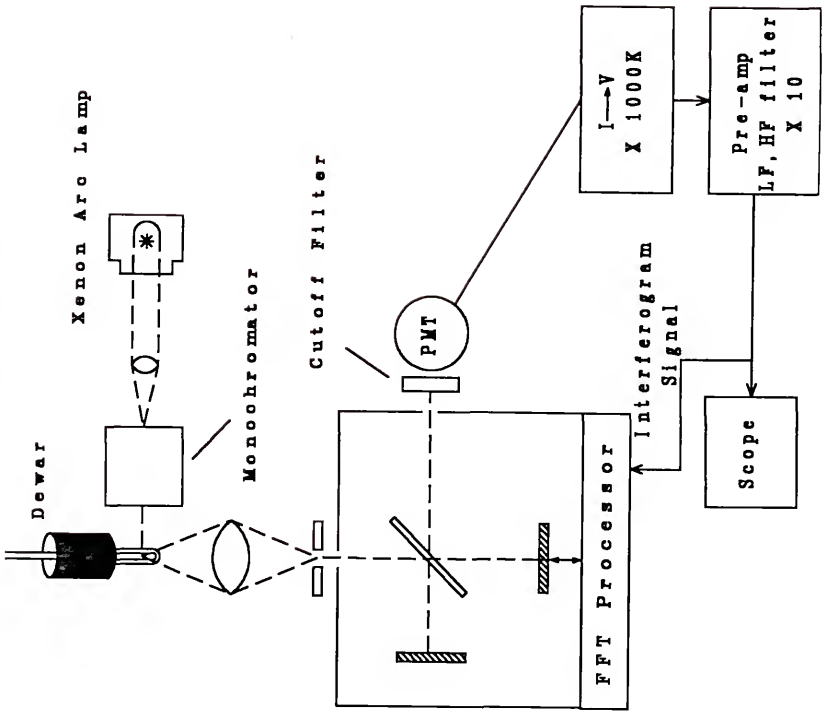

Figure 5. Schematic of molecular fluorescence emission setup.

were frozen by quickly immersing them in the liquid nitrogen. A 3-in focal length quartz lens focused the fluorescence emission on the 1 cm aperture at the entrance port of the interferometer (DA3.02, Bomem Inc., Vanier, Quebec).

An appropriate, long-pass, cutoff filter was used at the exit port of the interferometer to eliminate scattered excitation radiation. A photomultiplier tube (R647, Hamamatsu, Bridgewater, NJ) detected the radiation.

For the acquisition of fluorescence excitation spectra, the experimental setup was changed to place the sample after the interferometer. A schematic diagram of the system is shown in Fig. 6. The source was a 150 W compact xenon-arc lamp. For all measurements, a water filter was used to remove infrared radiation, and two Schott filter glasses (UG11) were used to remove the visible radiation. A 2-in focal length quartz lens focused the ultraviolet radiation on the 1 cm aperture at the entrance port of the interferometer.

The quartz Dewar flask, filled with liquid nitrogen, was placed at the focal point in the sample compartment of the interferometer. A quartz tube containing about 1 mL of the sample was quickly immersed in the liquid N_2. A 1:1 image of the tube was focused onto the entrance aperture of the cooled photomultiplier tube (9789QB, Thorn EMI, Fairfield, NJ), operated at -25°C. For coronene (Fluka, Ronkonkoma, NY) and anthanthrene (Aldrich, Milwaukee, WI), a 440 nm interference filter (S10-440) with a 10 nm bandpass and a long pass cut-off filter (LG 420) were used to allow only a particular fluorescence emission band to reach the detector. For benzo(a)pyrene and benzo(ghi)perylene (Aldrich), different interference

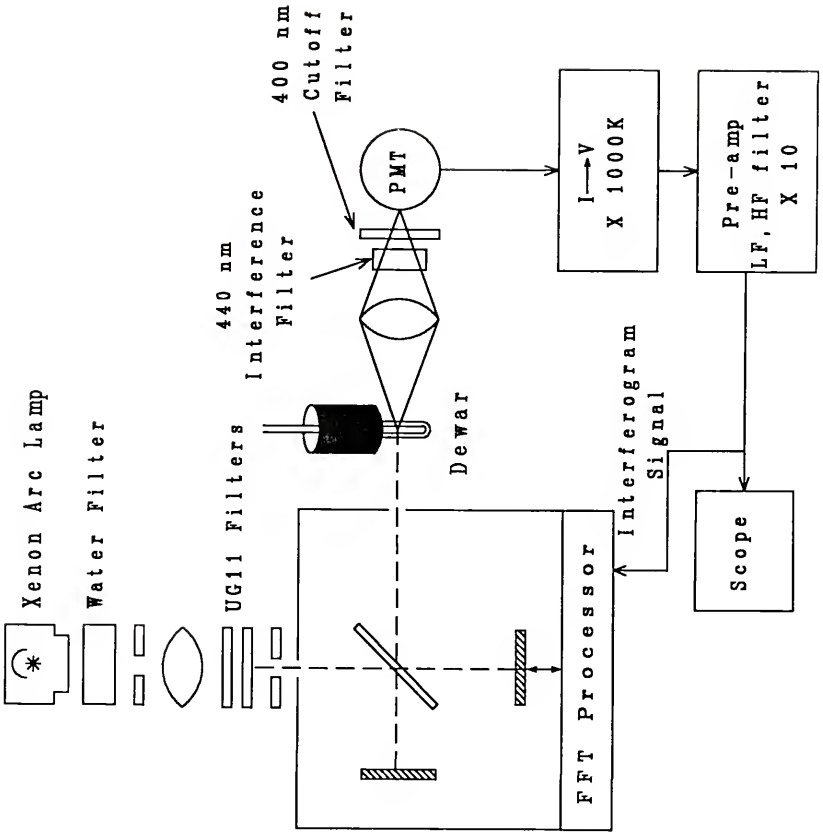

Figure 6. Schematic of molecular fluorescence excitation setup.

filters (10 nm FWHM) were used having transmission maxima at 420 nm and 450 nm, respectively.

All filters were obtained from Corion Corp. All solutions were prepared in UV-grade heptane or hexane (Burdick and Jackson, Muskegon, MI).

The interferogram signals from the photomultiplier tubes were amplified with a transimpedance amplifier (Model A1, Thorn EMI Gencom Inc., New York, NY), and then filtered and amplified with a pre-amp (Model 113, Princeton Applied Research, Princeton, NJ). The interferogram was viewed on an oscilloscope and sent to the interferometer's analog-to-digital convertor for processing.

Each spectrum was obtained by coadding 3000 interferograms with an instrumental resolution of 20 cm^{-1}. The scan rate of the mirror drive was 0.15 cm/s.

Results and Discussion

Figure 7 is an emission spectrum of perylene acquired with the Fourier transform setup shown in Fig. 5. The spectrum shows the characteristic narrowing that occurs in frozen Shpol'skii solvents. The half-width of the narrowest peaks is approximately 0.5 nm. For the acquisition of the perylene emission spectrum, the monochromator was set to allow a band of radiation at 400 nm to strike the sample. A 420 nm cutoff filter (50% transmission at 420 nm) was used to minimize the scattered excitation radiation reaching the photomultiplier tube.

The greatest drawback in this experimental design is the need to change the cutoff filter every time the excitation radiation changes. For other

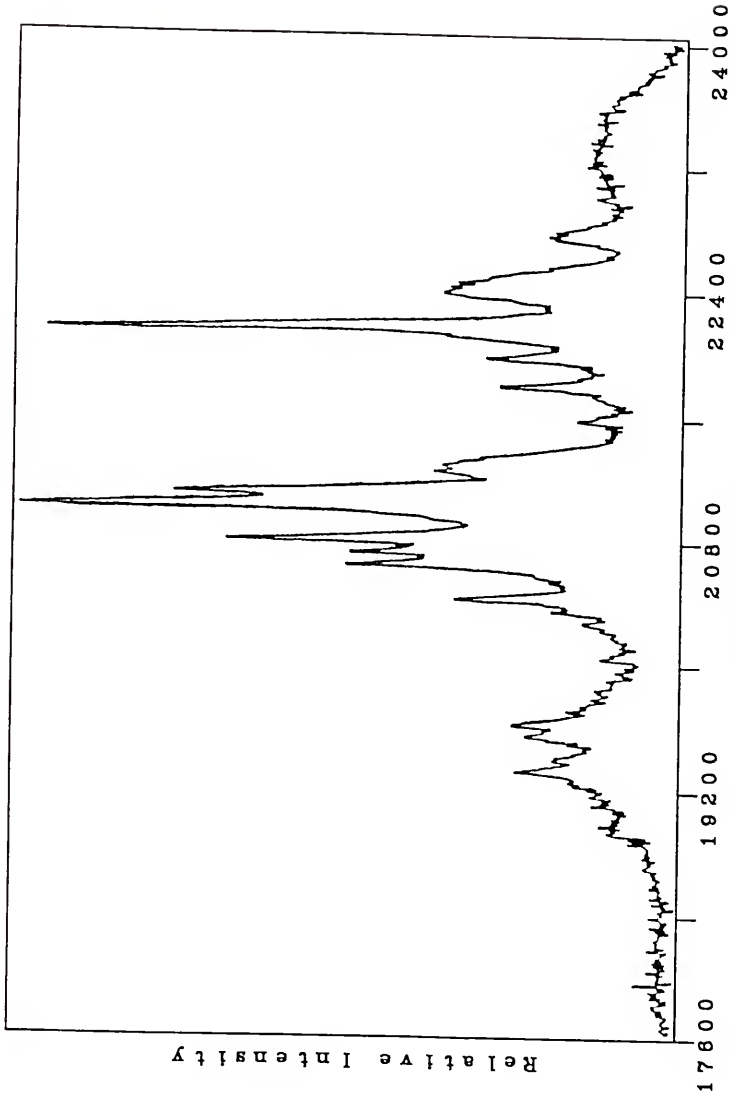

Figure 7. Emission spectrum of perylene at 77K.

PAC with different excitation spectra the monochromator must be set to the excitation maximum and the cutoff filter must be changed.

The signal-to-noise ratio for the emission spectra was poor due to the multiplex effect from all of the radiation striking the photomultiplier tube at one time. The emission spectrum in Fig. 7 was for a sample of 200 ppm perylene.

Realizing that the system was shot noise limited, and that multiplexing the radiation actually resulted in a reduction of signal-to-noise ratio, the second system shown in Fig. 6 was chosen for further evaluation. By placing the sample after the interferometer, excitation spectra could be acquired. With this setup there was no need to change the cut-off filter for different PAC because the same portion of the fluorescence emission was collected.

Since photon shot noise was the limiting source of noise in this study, attempts were made to reduce the bandwidth of radiation reaching the photomultiplier tube. The selection of the Schott filter glasses was made to reduce the excitation light to the region below 400 nm. Stray light below 400 nm which would reach the detector would not only contribute to the noise on the excitation spectrum, but would also appear as signal. Rejection of the stray light was achieved by using a 420 nm long pass cut-off filter at the detector.

A broad excitation bandpass was chosen to take advantage of the multichannel capability of Fourier transform spectrometry, although it was limited to the radiation passed by the Schott glass. The excitation spectrum was obtained by passing the radiation through the interferometer to the frozen sample and then measuring the fluorescence. The spectra

obtained for the four PAC are shown in Fig. 8. Only coronene exhibits the line-narrowing expected from the Shpol'skii effect. One explanation for the broad excitation spectra observed for benzo(a)pyrene, benzo(ghi)perylene, and anthanthrene may be found from symmetry considerations. The coronene molecule is highly symmetrical and therefore may exist in the frozen, n-alkane, crystalline matrix in only a few orientations. Having lower symmetry, the other three molecules undoubtedly occupy a larger number of sites in the matrix. Since the samples are illuminated with a broad band of ultraviolet radiation, all of the sites are equally excited, and the resulting spectra are broad. This broadening was not observed in fluorescence emission spectra where narrow excitation bands were employed.

Analytical figures of merit were determined for coronene frozen in the Shpol'skii matrix (Table 2). The calibration for coronene yielded a response with a linear dynamic range covering more than three orders of magnitude, with a log-log slope of 0.972. The detection limit was calculated as the concentration corresponding to a signal equal to three times the standard deviation of the blank. The standard deviation of the blank was taken as one-fifth of the peak-to-peak noise in the blank spectrum at the wavenumber of interest. The detection limits reported from the literature were determined using wavelength-dispersive fluorescence spectrometers.[28,29]

The detection limits for the Fourier transform measurements are better than those from dispersive instruments. Several explanations can be given for the increased sensitivity. For the Fourier transform measurements, a higher source intensity reaches the sample, since no dispersive device

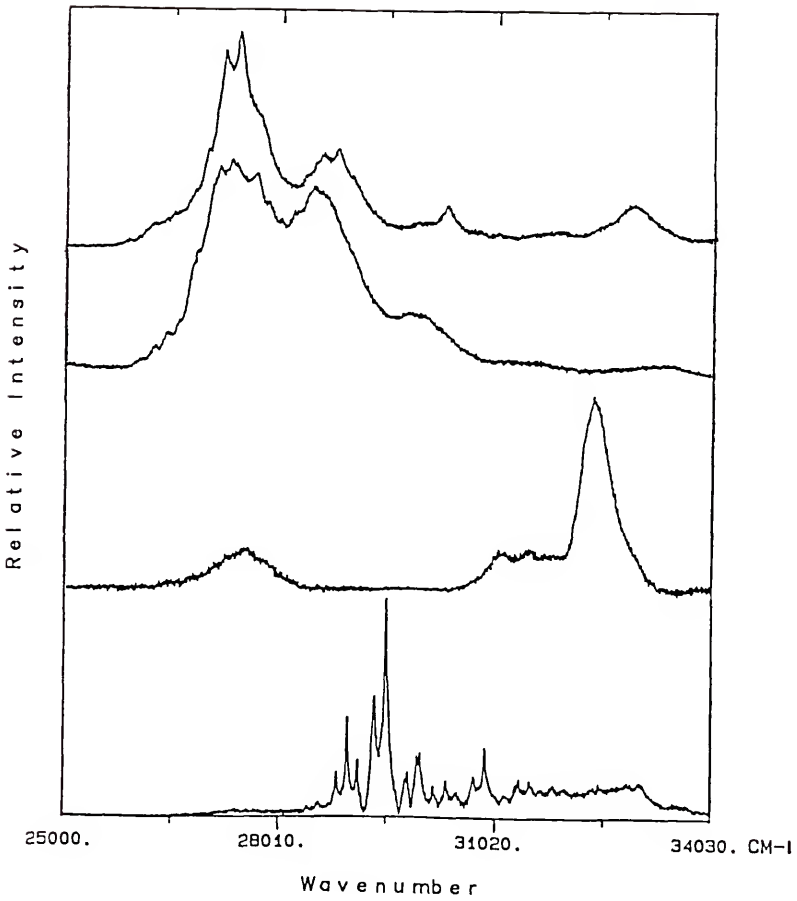

Figure 8. Excitation spectra at 77K. Top to bottom: benzo(a)pyrene, benzo(ghi)perylene, anthanthrene, coronene in hexane.

TABLE 2

Analytical Figures of Merit for Coronene
Frozen in Shpol'skii Solvent.

Wavelength Discrimination Technique (Temperature)	Excitation Maximum cm^{-1} (nm)	Detection Limit ng/mL (ng)	Linear Dynamic Range Orders of Magnitude	Precision %RSD
FT (77 K)	29486 (339.14)	2 (0.4)	3.2	12.6
Grating Spectrometer (77 K)[28]	29400 (340)	100 (3)	-	3.7
Grating Spectrograph (15 K)[29]	29700 (337)	20 (1)	3.0	7.6

is employed. A wider fluorescence bandwidth (10 nm) is allowed to reach the detector through the interference filter. In addition, many coadditions were made at each point on the calibration curve.

Figure 9 demonstrates the ability of this experiment to obtain directly the spectrum of the excitation source. With the cut-off and interference filters in place at the detector, the quasi-linear spectrum of coronene was observed. The interference filter had the effect of reducing the photon shot noise since the detector viewed less radiation. It also blocked significant phosphorescence emission of coronene which would have skewed the spectrum because of its long lifetime. The source spectrum was obtained by removing the cut-off and interference filters at the detector.

Figure 9 also shows a limitation with this instrumental set-up. Since the UG11 interference filter was used on the light source, only those analytes with excitation peaks in the region between 26,000 and 32,000 cm^{-1} could be reliably detected. This limitation could be eliminated by placing a low-resolution diffraction grating between the source and the interferometer. This allowed the source spectrum to be matched to the excitation bands.

No signal-to-noise multiplex advantage can be cited as motivation for molecular studies of this kind, but other potential advantages have been suggested. The multichannel capability of Fourier transform spectrometry can only be utilized by allowing a large window of radiation to pass through the interferometer. For absorption and fluorescence emission measurements, an increase in the shot noise would result. In this study, excitation spectra were obtained by measuring the fluorescence emission.

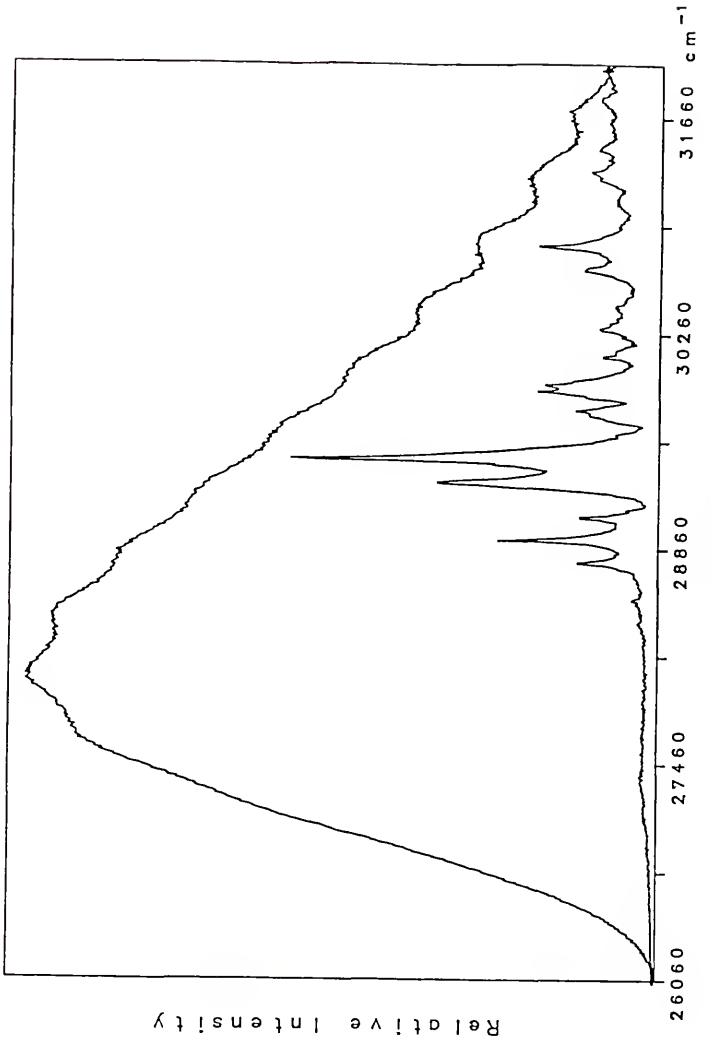

Figure 9. Excitation spectrum of coronene in hexane at 77K. The source profile is shown above.

By using a 10 nm bandpass interference filter, which limited the radiation reaching the detector, the shot noise was reduced, but the multichannel capability was retained because all of the excitation band was allowed to pass through the interferometer.

The high speed of spectrum acquisition using Fourier transform spectrometry has also been suggested as an advantage of using an interferometer in the ultraviolet-visible region. Even with the limited spectral window used in this study, defined by the interference filter, the signal-to-noise ratio was sufficiently poor that coaddition of interferograms for several minutes was necessary. The acquisition of dense spectra such as fluorescence excitation spectra has a multiplex disadvantage which requires long integration times.

Stray light is only a minor problem, since only modulated light which passes through the interferometer is interpreted as signal. This reduces the need for stringent protection of the detector from room light, although stray light may contribute to the shot noise. Computer manipulation of spectra is one inherent advantage to collecting spectra digitally, and the ease of obtaining a source spectrum makes it possible to acquire corrected excitation spectra.

The photon shot noise that limits Fourier transform studies is not as significant in dispersive spectrometry because it is largest where the signal is the highest. In dispersive spectrometry, the shot noise can be reduced significantly by electronic low-pass filtering. However, in Fourier transform spectrometry, the discriminate filtering of higher frequencies is limited by the sampling rate of the interferogram acquisition. The sampling rate is determined by the speed of the moving

mirror. The Bomem interferometer uses HeNe laser fringes for reference and takes 8 samples/fringe to acquire the interferogram. With a mirror movement of 1.0 cm/s, the sampling frequency is 253 kHz, which prevents high-frequency filtering below 500 kHz. At a mirror velocity of 0.01 cm/s, the sampling frequency is 2.53 kHz, allowing a 5 kHz high-frequency rolloff. The reduction in noise is a factor of 10, but the analysis time increases by a factor of 100. Furthermore, at such low scan rates, the ability of the interferometer to keep the mirrors aligned is degraded.

The use of Fourier transform spectrometry for the acquisition of low-resolution, spectrally-dense molecular spectra has disadvantages. The multiplex effect of always viewing the total photon shot noise spreads the noise throughout the spectrum, resulting in a lower signal-to-noise ratio compared to a dispersive system. The multiplex disadvantage is serious in regions of low intensity. To overcome this effect, long integration times are essential, effectively negating any speed advantage of Fourier transform spectrometry that might have been possible.

The analytical figures of merit determined for coronene compare well with those which have been obtained with conventional instrumentation, but since the noise at the wavenumber of interest can be affected by radiation in other regions of the spectrum, the detection limits of this technique can be expected to degrade with increased sample complexity. Non-analyte signal reaching the detector will increase the noise. A sample pretreatment step such as solvent extraction or chromatographic separation would be required in such cases.

An alternative arrangement, with the sample before the interferometer and the fluorescence collected at the entrance port, showed poorer

results, since fluorescence emission at all wavelengths reached the detector simultaneously. The increased photon shot noise in this case resulted in greater noise. This problem could be eliminated at the expense of losing multichannel information by placing a monochromator at the exit port of the interferometer, thereby reducing the spectral window at the detector from approximately 100 nm to 10 nm or less. In this case, a slew scan technique to obtain the entire emission spectrum could be employed as was done by Horlick et al[24] and suggested by Winefordner et al.[8] An advantage of this arrangement would be the added selectivity resulting from the wavelength tunability at the source. A broad excitation band would not be required and more conventional Shpol'skii spectra should be observed.

FOURIER TRANSFORM ATOMIC ABSORPTION SPECTROMETRY

Introduction

Atomic absorption spectrometers are commercially available only with atomic line sources. A requirement of these instruments is a separate source for each element—a drawback that complicates multi-elemental analysis. This approach increases the cost of the system and demands optical alignment each time the lamp is changed. To avoid these complications, atomic absorption with a continuum source has been investigated.

Even in the first description of the atomic absorption method in 1955, the use of continuum sources was suggested.[30] An intense continuum source in atomic absorption would mean that one lamp could be used for the determination of all elements. Alignment problems and cost would be reduced. However, to achieve high sensitivities, continuum sources were abandoned for spectral line sources.

The sensitivity of an atomic absorption method depends on the effective spectral bandwidth of the excitation radiation relative to the absorption line.[31,32] For conventional line source atomic absorption, the effective spectral bandwidth is determined by the width of the atomic emission line in the source. When continuum sources are used, the monochromator determines the effective spectral bandwidth. To achieve the sensitivity of line source atomic absorption when a continuum source is used,

effective spectral bandwidth of the monochromator must approach the bandwidth of the atomic absorption line. Much work on the development of continuum source atomic absorption dwells on the achievement of this spectral resolution.

Several approaches have been taken. High resolution spectrometers and high resolution interferometers have been used to provide the narrow spectral bandwidth required in continuum source atomic absorption. To compete with conventional atomic absorption methods, the newer methods must have comparable detection limits and simple instrumental requirements.

High resolution Fabry-Perot interferometers have been used with continuum sources.[33,34] Effective spectral bandwidths approaching those of line source methods were achieved, but significant disadvantages appeared. The use of Fabry-Perot interferometers is more complicated, and optical alignment is critical. To take advantage of the wide spectral coverage of continuum sources, the interferometer must be capable of operation over a wide range. Fabry-Perot interferometers, however, have limited use because of the lack of highly reflective materials that cover a wide spectral range. In addition, medium resolution monochromators are often needed to allow only a portion of the spectral range to enter the interferometer.

High resolution, dispersive spectrometers have been used to provide the required resolving power. Echelle-grating spectrometers are the most practical and have been used in many investigations.[35-37] Effective spectral bandwidths equal to line source atomic absorption can be achieved, and simultaneous, multi-element determinations are possible.

The majority of current research in continuum-source atomic absorption is based on echelle-grating spectrometer systems.

Other approaches have been taken to achieve high resolution. Spectral line modulation[38] and sample modulation[39,40] have been used with medium resolution monochromators. Resonance monochromators have also been used to decrease the effective spectral bandwidth.[41-43]

Of all the methods, the use of echelle-grating spectrometers has been the most successful and is the subject of several reviews.[44-46] Detection limits for more than thirty metals are usually a factor of 2 poorer than those of line-source atomic absorption. Alternative approaches to using a continuum source must be compared to this method.

The Michelson interferometer has been suggested as a component in an atomic absorption spectrometer with a continuum source.[8,17] Fourier transform spectrometry has the advantages of high spectral resolution, wavelength accuracy, and high throughput. Sensitivities of an approach using a Michelson interferometer should be comparable to those of other continuum-source methods. The wide spectral coverage of the interferometer should yield complete absorption spectra.

The disadvantages of Fourier transform spectrometry in the ultraviolet-visible region have already been documented here and in the literature.[8,26,27] Because the system is photon shot noise limited in that region, the multiplex advantage is not realized. Dense spectra, in which radiation over a wide range is present, should even show a multiplex disadvantage.[20,47]

This investigation was to determine whether the advantages of Fourier transform spectrometry in continuum-source atomic absorption will

compensate for the expected disadvantages of Fourier transform spectrometry in the ultraviolet-visible region. A commercial Michelson interferometer was used for atomic absorption measurements in a flame. A predispersing element was used to select a spectral window around the atomic line of interest. Multi-element determinations were performed for elements within the spectral window. Detection limits for several elements are given. Background correction is possible because absorption spectra are acquired. A single source can be used for the determination of many elements, and linear calibration curves can be extended by using the absorption profile.

Experimental

Two experimental setups were used in this investigation. In the atomic absorption spectrometer shown in Fig. 10, the flame was placed after the interferometer. Radiation from the continuum source was focused on an iris diaphragm, and then collimated by a second quartz lens. The collimated radiation was dispersed by a plane-ruled grating, and a third lens collected a portion of the radiation and focused it on the entrance port of the interferometer.

Collimated radiation from the exit port of the interferometer was passed through the flame directly onto the photomultiplier tube, as shown in Fig. 10, or was directed with quartz prisms to the photomultiplier tube 4 ft away from the flame.

In the second setup, the flame was placed before the interferometer. A diagram of the atomic absorption spectrometer is shown in Fig. 11. Radiation from the continuum source was passed through the flame without

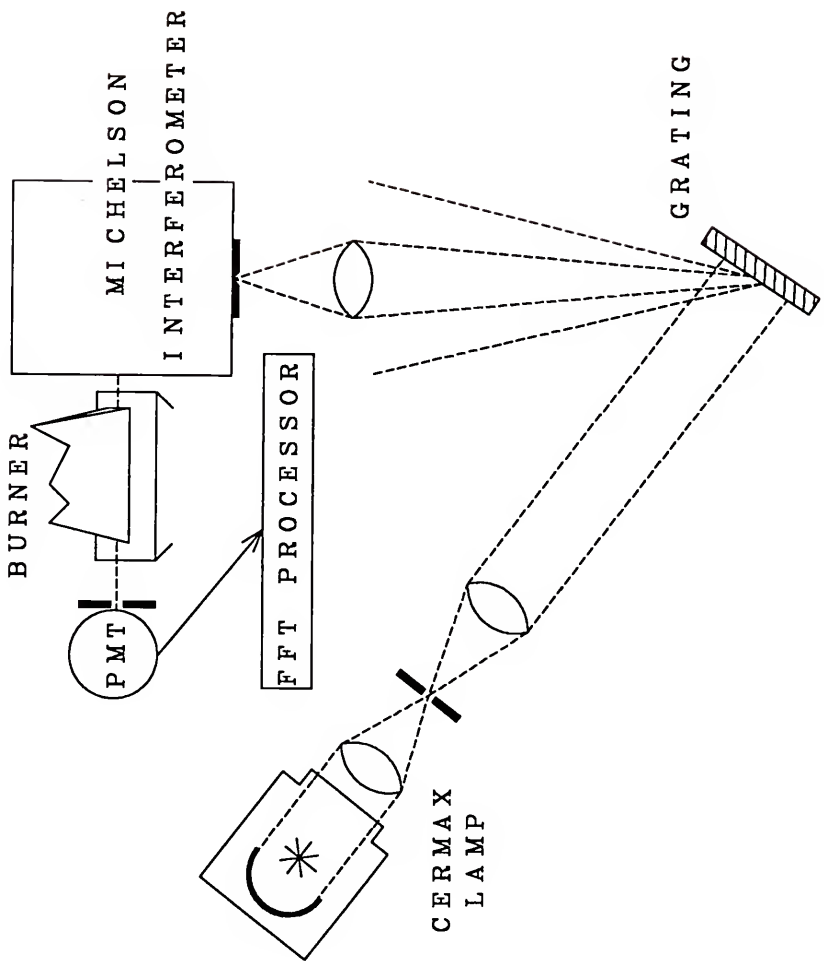

Figure 10. Schematic of first atomic absorption setup.

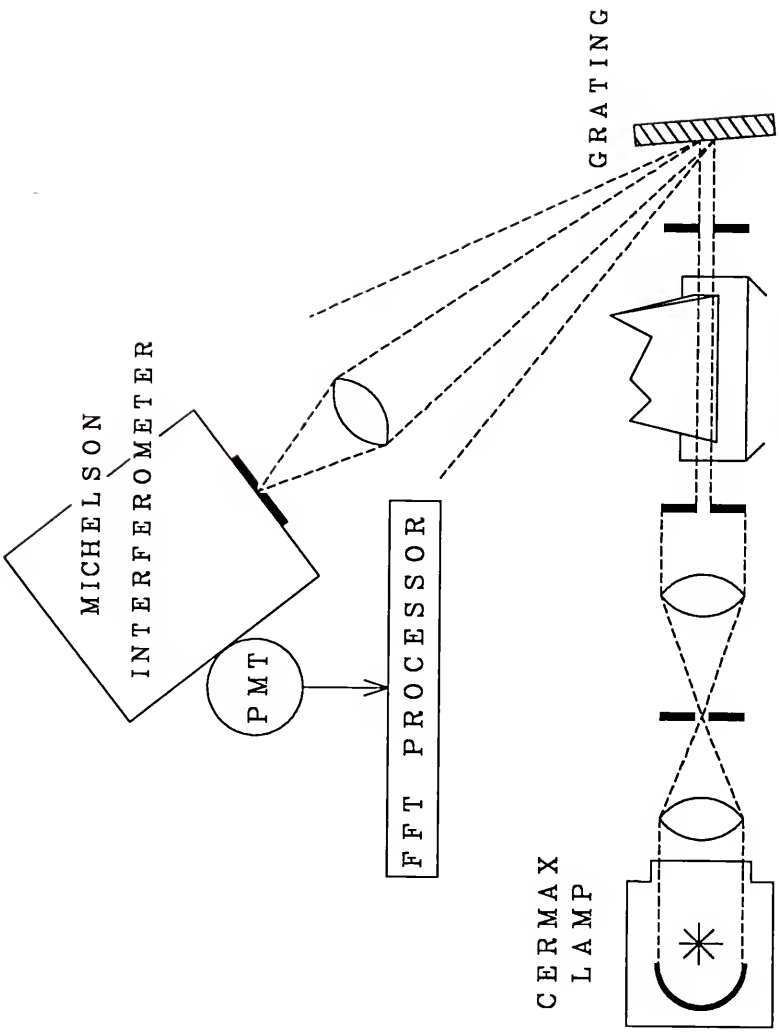

Figure 11. Schematic of second atomic absorption setup.

any spectral dispersion. A lens was used to focus the radiation from the lamp on an iris diaphragm, before collimation by a second lens. A second iris diaphragm allowed only a portion of the collimated radiation from the less turbulent region of the lamp image to pass through the flame.[48] After the flame and before the interferometer, a grating was used to disperse the radiation. A quartz lens focused a portion of the dispersed radiation onto the entrance port of the interferometer.

The Michelson interferometer (DA3.02, Bomem, Vanier, Quebec) in these setups was commercially available and used without modification. A photomultiplier tube (R647, Hamamatsu, Bridgewater, NJ) was used for detection of the interferogram. The source of radiation was an unfiltered, 300 W xenon arc lamp (Cermax, ILC Technologies, Sunnyvale, CA). Predispersion of the radiation was accomplished by a 2400 gr/mm, plane-ruled grating, blazed at 300 nm (SLM-Aminco, Urbana, IL). The grating could be rotated to select the radiation window of interest, which was focused onto the entrance aperture of the interferometer. The spectral halfwidth of the source radiation entering the interferometer was approximately 5 nm.

The fuel-lean air/acetylene flame was produced by a 10-cm slot burner (Perkin Elmer, Norwalk, CN). Collimated white light, stopped to 1 cm dia., passed through the flame to the grating. In both designs, an aperture was used to reduce the collection of flame emission.

Each absorption measurement was made by recording a reference spectrum with 1.00 cm^{-1} resolution, unless otherwise indicated. One hundred interferograms were added for both reference and absorption spectra. The scan rate of the interferometer was 0.15 cm/s, for an average time of

spectrum acquisition of 10 min. Even at concentrations as high as 10 mg/mL, no analyte emission could be detected with the optical configuration shown in Fig. 11.

Results and Discussion

A grating was used for predispersion of the radiation entering the interferometer to limit the window of radiation striking the detector. In the photon shot noise limited region, predispersion resulted in an increase in the signal-to-noise ratio, because the photon flux at the detector is reduced. This limited the spectral region that could be used for multielement analysis to 5 nm. The entire absorption spectrum in that window could be obtained by the interferometer, but unlike echelle-grating systems, multiple lines at discontinuous spectral regions cannot be simultaneously measured.

Gratings with poorer dispersion could be used to obtain a larger spectral window, which would permit the acquisition of absorption spectra over an even wider range. The larger spectral window, however, would also increase the radiation at the detector and degrade the signal-to-noise ratio.

To demonstrate the multiplex disadvantage, the effect of photon flux at the detector on the signal-to-noise ratio of sodium absorption lines was investigated. The Bomem interferometer uses an internal HeNe laser for alignment, which strikes the photomultiplier tube. To attain a spectrum with high signal-to-noise ratio, the HeNe laser radiation was spatially blocked at the exit port of the interferometer. In Fig. 12, Case I shows the relative intensity of the HeNe laser radiation that could

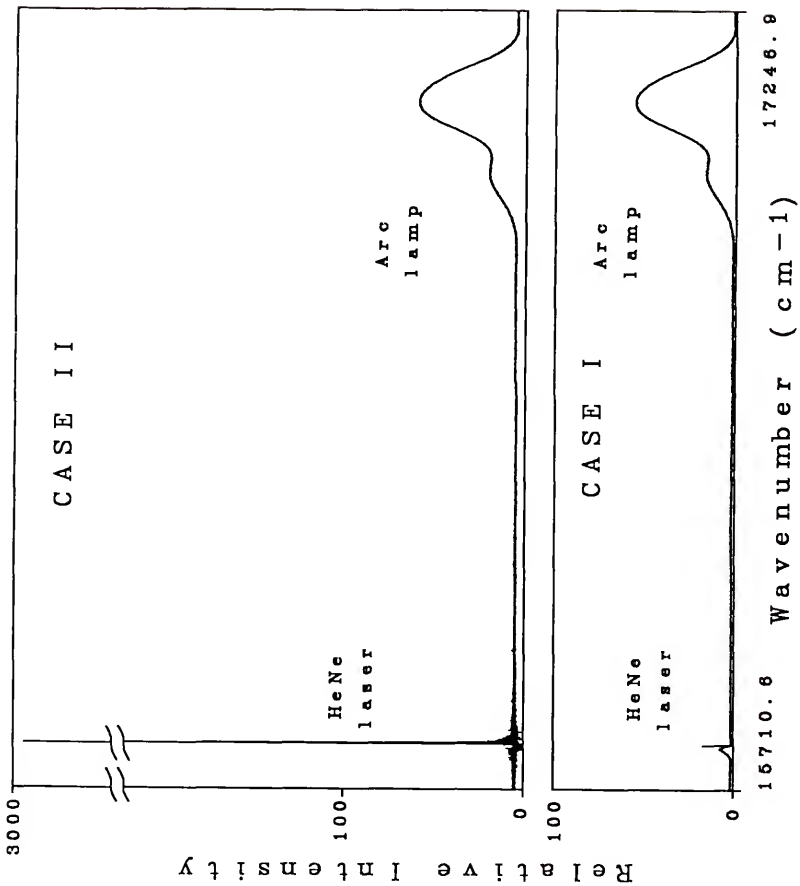

Figure 12. Relative intensities of HeNe laser radiation in multiplex experiment.

not be blocked, in comparison to the excitation radiation from the continuum source. For Case II, the internal laser radiation was not blocked, and an external HeNe laser was also used to increase the photon flux striking the detector. In Case II of Fig. 12, the laser radiation has a peak intensity almost 200 times that of Case I. The excitation radiation was not changed.

The effect on signal-to-noise ratio of the absorption spectrum of the sodium doublet is shown in Fig. 13. The poorest signal to noise is obtained in Case II, when the HeNe laser radiation is much more intense than the excitation radiation. The noise from the HeNe laser radiation was distributed over the analytical lines. Unfortunately, the radiation from the internal laser cannot be blocked entirely, and inevitably it reaches the photomultiplier tube. In the shot noise limited region, this contributed to a multiplex disadvantage. A solar-blind photomultiplier tube would avoid this particular problem.

Detection limits for several elements with lines in the ultraviolet and visible region are shown in Table 3. The detection limits are at least an order of magnitude poorer than those which have been obtained by an echelle-grating spectrometer and continuum source. The same trend of poorer detection limits as the analytical line moves to shorter wavelengths that is observed in other continuum source AAS methods was observed here.

To determine the cause of the poorer detection limits, the sensitivity and noise of the system were investigated. The sensitivity is related to the effective spectral bandwidth and in this system is determined by the mirror movement of the interferometer. Table 4 lists elements frequently

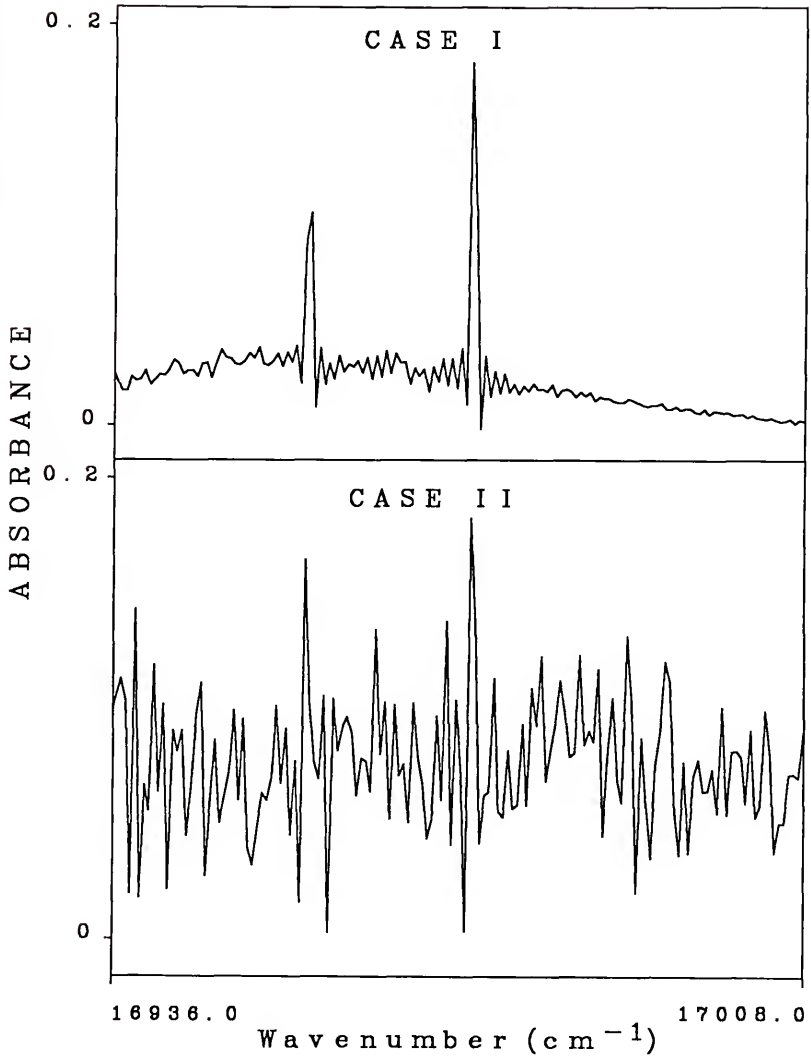

Figure 13. Comparision of signal to noise in multiplex experiment.

TABLE 3

Detection Limits for Fourier Transform, Atomic Absorption with a Continuum Source

Element	Wavelength (nm)	Detection limit (μg/mL) FT	Dispersive[46]
Ag	328.068	0.2	0.007
Cu	324.754	0.1	0.01
Mn	279.482	0.2	0.01
Na	588.995	0.02	0.003

TABLE 4

Atomic Absorption Lines and Widths

ELEMENT	λ (nm)	$\Delta\lambda$ (pm)
Antimony	217.6	1.1
Arsenic	193.7	1.1
Beryllium	234.9	3.4
Cadmium	228.8	1.2
Calcium	422.7	4.1
Chromium	359.4	2.9
Cobalt	242.5	1.6
Copper	324.7	2.4
Gold	242.8	1.1
Iron	248.3	1.7
Lead	217.0	0.9
Lithium	670.8	17.
Magnesium	285.2	2.8
Manganese	279.5	2.0
Mercury	253.6	1.2
Nickel	232.0	1.5
Platinum	265.9	1.2
Potassium	766.5	11.
Selenium	196.0	1.0
Silver	328.1	2.0
Sodium	588.9	8.2
Tellurium	214.2	1.0
Thallium	377.6	2.2
Zinc	213.9	1.3

determined by continuum source atomic absorption and the half-width of the most prominent lines. The highest sensitivity will be achieved when the lines are fully resolved. Fig. 14 shows the effect of instrumental resolution on the measured absorbance at the 327.396 nm line of copper. As the spectral bandwidth decreases, the observed peak absorbance increases, until the bandwidth is less than that of the line. Below an instrumental resolution of 0.03 Å the absorbance does not change.

All absorbance measurements made for the determination of the detection limits in Table 3 were made with an instrumental resolution of 1.00 cm^{-1}, at the copper line this corresponds to 11 pm. Although this resolution did not result in maximum absorption, it was chosen as a compromise. Much longer spectrum acquisition times would have resulted if better resolution was selected. An instrumental resolution of 3 pm would yield a higher absorbance for copper, but the time of acquisition would become prohibitive.

One advantage that is realized to some extent is the multichannel capability. Atomic absorption spectra can be obtained over the profile of the line, as long as the line falls within the selected window of radiation entering the interferometer. This would allow the use of the profile of the absorption line for diagnostic purposes, background correction, and for extension of the calibration curve. The capability of extending the linear range of the calibration curve has been demonstrated with continuum source AAS.[49,50] The automatic acquisition of the absorption spectrum that is possible with this system also allowed this type of extension. Figure 15 shows the extension of the linear portion of a calibration curve for sodium. Absorption measurements were

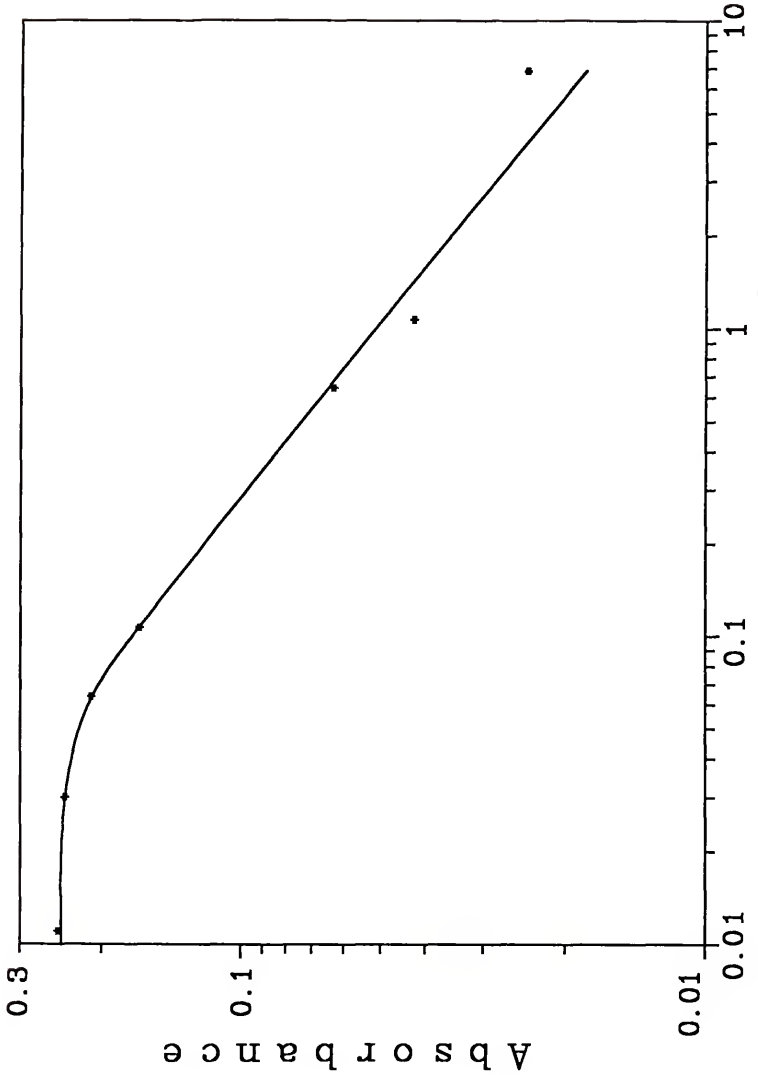

Figure 14. Effect of resolution on analytical sensitivity.

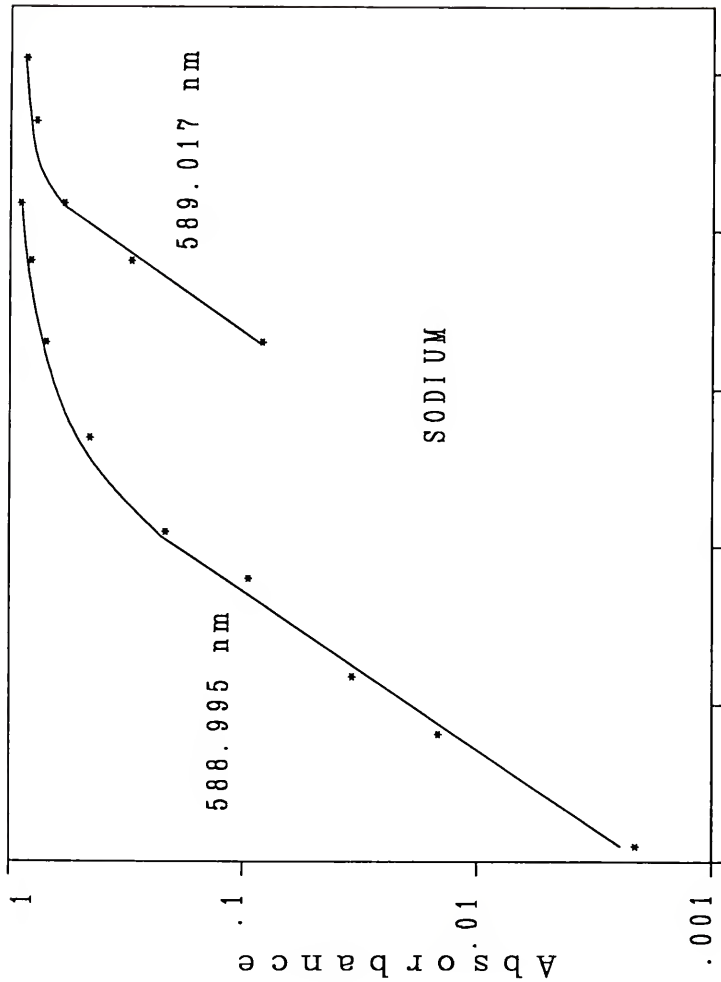

Figure 15. Extension of sodium calibration curve by off-peak measurements.

taken from the spectrum at the peak of the line profile and on the edge of the line profile.

The limited multielement capability is demonstrated by the absorption spectra of Fig. 16 and Fig. 17. Four absorption peaks corresponding to 100 μg/mL of three elements, Cu, In, and Ag, are shown in Fig. 16. At shorter wavelengths, four absorption peaks corresponding to 100 μg/mL of two elements, Mn and Mg, are shown in Fig. 17. The analytical use as a simultaneous multielement method is limited, because only those elements which happen to have absorption lines within the 5 nm spectral window will appear in the spectrum. The use of a grating with poorer dispersion would allow the simultaneous determination of more elements, but signal-to-noise ratio would decrease due to the increased total light flux reaching the photomultiplier tube.

Fourier transform atomic absorption spectrometry with a continuum source is limited as an analytical technique since the spectral range, sensitivity, detection power, and acquisition time are interdependent and limited. Nevertheless, the technique may have limited use in specialized analytical applications, especially where ease of background correction and line identification are important, and where several selected elements must be measured simultaneously.

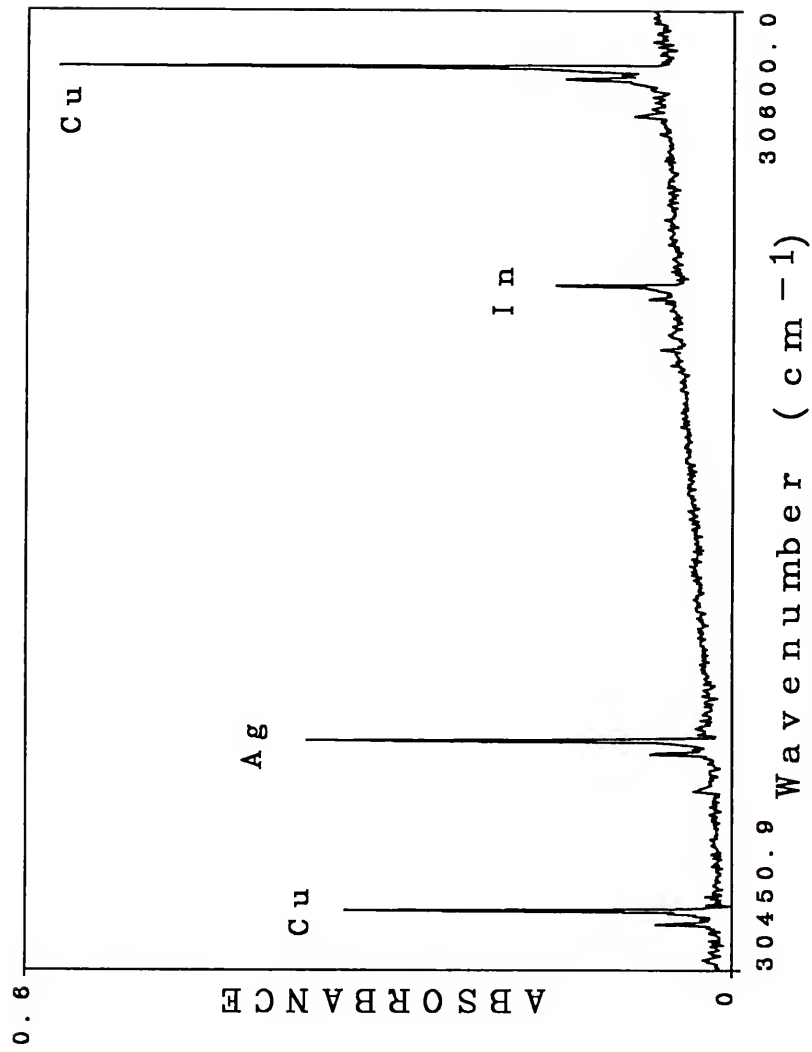

Figure 16. Absorption spectrum of 100 ppm standard mixture of copper, silver, and indium.

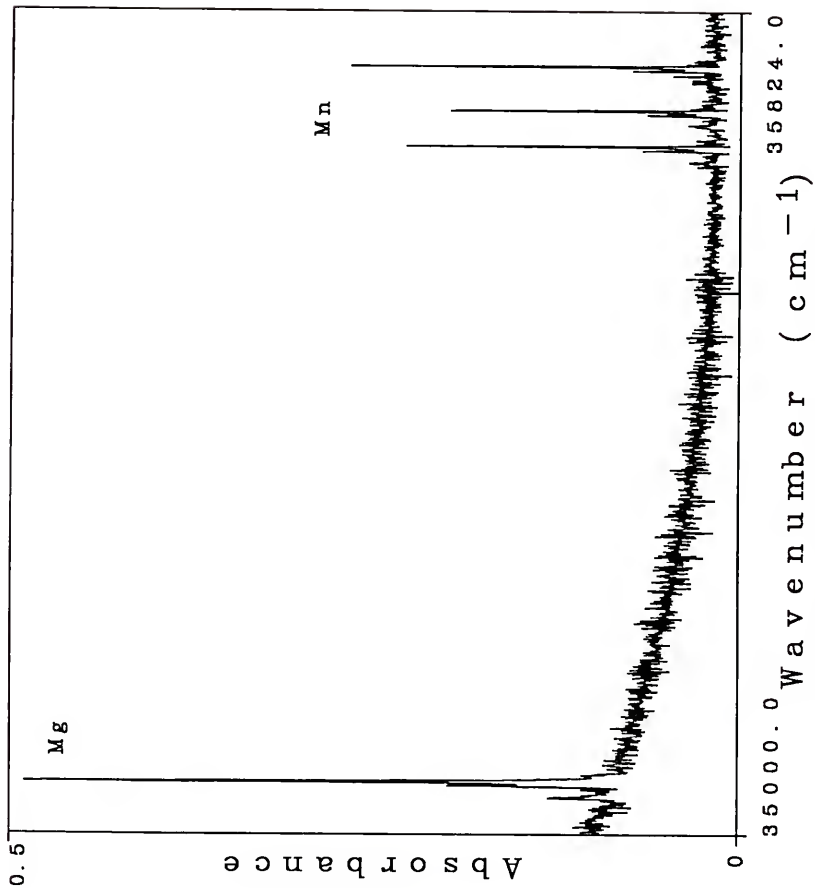

Figure 17. Absorption spectrum of 100 ppm standard mixture of magnesium and manganese.

CONCLUSIONS

The analytical use of Fourier transform spectrometry in the ultraviolet-visible region has been investigated. Five spectrometric systems using a Michelson interferometer were constructed and evaluated. Molecular absorption spectra were acquired by using a dispersion grating before the interferometer to select a window of radiation. Pseudo-line, fluorescence excitation and emission spectra of polycyclic aromatic hydrocarbons frozen in a Shpol'skii solvent were obtained. The Michelson interferometer replaced the spectrometer in a conventional setup. Atomic absorption spectra were acquired by using a continuum source for excitation and a dispersive grating before the interferometer.

Detection limits for the absorption study were predictably poorer than in a conventional system. A preliminary investigation using a continuum source without any spectral discrimination before the interferometer showed that the signal-to-noise ratio of the measurement was degraded by the multiplex effect. Attempting to reduce this effect, a predispersing grating was used before the interferometer, allowing only 70 nm of radiation. This improved the signal-to-noise ratio, but coaddition of interferograms was still necessary for satisfactory results. The greatest advantage of Fourier transform spectrometry in the ultraviolet-visible region, the high resolving power, is not used in a molecular study of this type. The greatest disadvantage, the degradation of signal-to-noise ratio

by the multiplex effect, makes this spectrometric system of limited analytical use.

Shpol'skii narrowed fluorescence emission spectra were acquired by placing the Dewar flask before the interferometer, using a low-resolution monochromator for selecting the excitation radiation. A long-pass cutoff filter was necessary at the detector to remove scattered excitation radiation. One of the drawbacks of this configuration was the need to change the cutoff filter for each change of excitation. This disadvantage, along with the poor signal-to-noise ratio that resulted from the multiplex effect of all of the emission radiation striking the detector, prompted a more thorough investigation of an alternative setup for the acquisition of fluorescence excitation spectra.

The main difference between the excitation setup and the emission setup is that for the acquisition of excitation spectra, the filters do not need to be changed. By using a Schott glass filter that passes radiation in the ultraviolet and covers the excitation spectra of most polycyclic aromatic hydrocarbons, one filter can be used for all determinations. A cutoff filter and interference filter were used at the detector to eliminate scattered radiation and to allow only a small fraction of the fluorescence to be detected. The effect is that the detector viewed only the fluorescence, the multiplex disadvantage was not prohibitive, and complete excitation spectra could be acquired.

Coaddition of spectra was still necessary to improve the signal-to-noise ratio, but detection limits were an order of magnitude better than those of a conventional system. The use of continuum source excitation also contributed to the excellent sensitivity. The spectrometric system

may be of use analytically because it can provide the high resolving power needed for some molecular studies. Unfortunately, by using continuum source excitation, the Shpol'skii effect was only observed for one sample, coronene, because other, less symmetrical molecules occupied many different sites in the frozen matrix. The continuum source excited all of the sites. For other molecular studies, e.g. gas-phase molecules, that require high resolution in the ultraviolet-visible, Fourier transform spectrometry may be of use. The multiplex disadvantage could be significant.

For the acquisition of atomic absorption spectra, two experimental configurations were used, both using a dispersive grating before the interferometer to reduce the multiplex disadvantage. Placing the flame after the interferometer prevented the background emission from modulation by the interferometer, but also located it closer to the photomultiplier tube. The bright flame emission was difficult to block at the detector, and the interferogram was an AC signal on top of a noisy, DC offset. To simplify the setup, the flame was placed before the interferometer for further investigation.

Although any emission reaching the interferometer would be modulated and appear as signal, by using collimated excitation radiation, the emission could be optically disregarded. The grating allowed only a 5 nm window of radiation to pass through the interferometer, which reduced the amount of information that could be obtained at once, but also reduced the multiplex disadvantage. The grating could be rotated to select the excitation window, and multi-element determinations could be performed if several atomic lines were within the same window.

Although limited analytically, the atomic absorption spectrometer constructed with the Michelson interferometer has a few advantages. The high resolution capability of the interferometer can be utilized for diagnostic purposes. The acquisition of complete absorption spectra can be used for true background correction, as well as an investigation of atomic line profiles. Calibration curves can be extended by using the entire line profile for their construction.

The Michelson interferometer is limited in its usefulness to routine analytical use in the ultraviolet-visible region. The multiplex effect results in a significant signal-to-noise degradation in many cases, especially where the spectral feature is weak and surrounded by other strong spectral signals. The throughput advantage that is cited in the infrared appears in the ultraviolet-visible region, but is often offset by the multiplex disadvantage.

Three other advantages, compared to dispersive spectrometers, could be of some analytical use. The wavenumber accuracy and precision of the interferometer permits the confident identification of spectral features in a complex spectrum. This advantage has already been realized in Fourier transform atomic emission studies. A second advantage that could be of use is the simultaneous coverage of a wide spectral range with high resolution, even better than a diode array. However, much of this advantage must be sacrificed for improvement of the signal-to-noise ratio. The multiplex disadvantage arises because of this feature. In these studies a predispersing element was often used to limit the spectral range of radiation entering the interferometer.

The third advantage is most important—the high resolving power of an interferometer. Resolution that is easily achieved by an interferometer, even in the ultraviolet-visible region, is possible only by the biggest conventional spectrometers. Only those analytical studies that require the high resolving power of the Michelson interferometer will use Fourier transform spectrometry in the ultraviolet-visible region.

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BIOGRAPHICAL SKETCH

Mark Glick was born in 1962. He attended Goshen College, Goshen, Indiana. He entered graduate school in 1985.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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